

# **An Integrated Hydrogen Production-CO<sub>2</sub> Capture Process from Fossil Fuel**

## **Semiannual Progress Report**

**Reporting Period Start Date: March 15, 2006**

**Report Period End Date: September 15, 2006**

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**Date Report Was Issued: September 2006**

**DOE Award Number: DE-FG26-03NT41914**

**Submitted by: Clark Atlanta University, Atlanta, GA 30314**  
**Eprida Scientific Carbons Inc., Atlanta, GA**

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## **ABSTRACT**

The major project objective is to determine the feasibility of using the char from coal and/or biomass pyrolysis, ammonia and CO<sub>2</sub> emissions at smokestacks to produce clean hydrogen and a sequestered carbon fertilizer. During this work period, the project plan, design and test schedules were made on the basis of discussion with partner in experimental issues. Installation of pilot scale units was finished and major units tests were fully performed. Modification of the pyrolyzer, reformer and gas absorption tank have been done. Integration testing is performing recently. Lab scale tests have been performed. Field tests of char/fertilizer have been conducted.

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## INTRODUCTION AND OBJECTIVES

The increasing anthropogenic CO<sub>2</sub> emissions and possible global warming have challenged the United States and other countries to find new and better ways to meet the world's increasing need for energy while, at the same time, reducing greenhouse gas emissions. The improved technology for integrated hydrogen production/CO<sub>2</sub> capture that we plan to develop through this R&D effort could significantly support President Bush's Global Climate Change Initiative (GCCCI) that commits America to an aggressive strategy to reduce greenhouse gas intensity by 18 percent over the next 10 years. Our new technology concept integrates two significant and complementary hydrogen production and CO<sub>2</sub>-sequestration approaches that have now been developed at Oak Ridge National Laboratory (ORNL) and Clark Atlanta University.

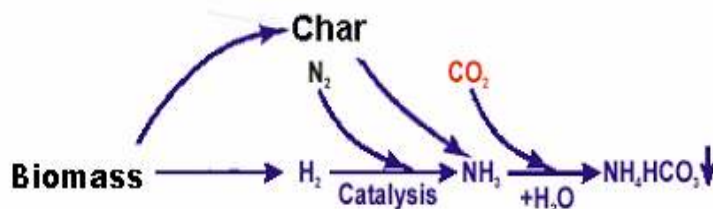


Figure 1 Schematic View of the process from Biomass to Fertilizer

Figure 1 illustrates the schematic view of the process of converting biomass into hydrogen and char. Hydrogen can be efficiently used for stationary power and mobile applications, or it can be synthesized into Ammonia, while char can be used for making time-release fertilizers (NH<sub>4</sub>HCO<sub>3</sub>) by absorption of CO<sub>2</sub> and other acid gases from exhaust flows. Fertilizers are then used for the growth of biomass

The objective of the proposed study is to determine the feasibility of using the char from a coal and/or biomass pyrolysis-reforming process and CO<sub>2</sub> emissions at a smokestack

to form a solid  $\text{NH}_4\text{HCO}_3$ -char product that may subsequently be used as a fertilizer. Part of the hydrogen from the pyrolysis-reforming process may be used to synthesize ammonia that is used to solidify the  $\text{CO}_2$  as  $\text{NH}_4\text{HCO}_3$  in the char. The balance of the hydrogen may be purified and sold at market prices or used as material for further products.

This project plans to conduct bench scale experiments and pilot scale tests. The Combustion and Emission Lab at Clark Atlanta University has prepared to conduct the bench scale experiments. The facility used for pilot scale tests has built in Athens, GA.

In This period, the effect of char without  $\text{NH}_4\text{HCO}_3$  on plants are evaluated. The evaluation of the fertilizer,  $\text{NH}_4\text{HCO}_3$  Char product, was conducted in lab.

## **EXPERIMENTAL FACILITIES**

Our integrated process consists of two stages: 1) pyrolysis of biomass to generate pyrolysis gas/char, and 2) catalytic steam reforming of pyrolysis gas. Figure 2 shows the schematic flow diagram of the developed process. The flow procedure of the process is as follows: Feeder accepts biomass; the pyrolysis unit pyrolyzes the biomass into pyrolysis gas and char at around  $500^\circ\text{C}$ ; char is leaked out at this stage, while pyrolysis gas flows into baghouse to filter out solid components accompanied with pyrolysis gas; before the gas is introduced into catalytic reformer, the pyrolysis gas is heated up to  $680^\circ\text{C}$ ; in the reformer at  $850^\circ\text{C}$ , most of pyrolysis gas is finally converted into hydrogen, carbon dioxide and water; after condensed and cooled down the water vapor, the mixtures of hydrogen and carbon dioxide, along with the nitrogen and other gases at normal temperature are produced. Hydrogen can be purified from the mixed gases. In our experiments, hydrogen is burned at the exit.

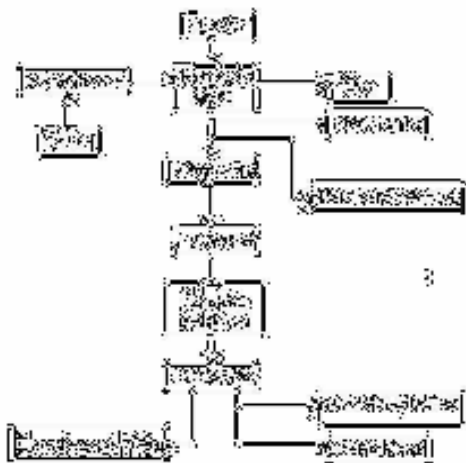


Figure 2 Schematic Flow Diagram of Char and Hydrogen Production

A photo of the pyrolysis unit of the pilot scale plant is shown in Figure 3. Char is led out from bottom of this unit.



Figure 3 Pyrolysis Unit with Biomass feedstack system

The next step after char produced is to make fertilizer. Figure 4 is the Schematic diagram of the bench scale experiments for  $\text{NH}_3\text{-CO}_2$  solidification. Before the  $\text{NH}_3$  and  $\text{CO}_2$  Introduce into the reactor, the char (activated carbon) needs to be mixed with water at various ratio and filled into the reactor. Then, the reactants ( $\text{NH}_3$  and  $\text{CO}_2$ ) flow into the reactor to

form a solid  $\text{NH}_4\text{HCO}_3$ -char product that may subsequently be used as a fertilizer. The flow rates of each gases are controlled by MKS flow controllers. The remaining Ammonia is absorbed in water bath Carbon Dioxide can be detected by Agilent Micro GC.

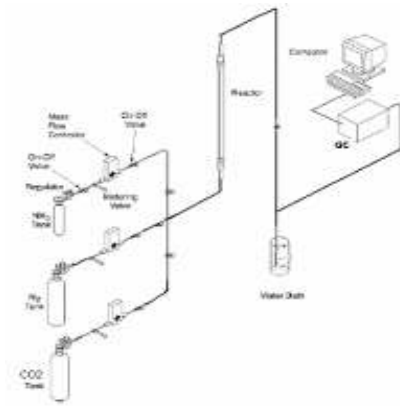


Figure 4 Schematic of Bench Scale Test of  $\text{NH}_3$ - $\text{CO}_2$  solidification

Figure 5 shows the fertilizer reactor for the bench scale experiments. The 1/3 reactor is filled with wet char (20g). After reaction, 3-7 gram of  $\text{NH}_4\text{HCO}_3$  can be formed.



Figure 5 Photo of Bench Scale Test



## RESULTS AND DISCUSSION

The Char and Hydrogen production experiments have been done. Figure 6 illustrates the dry  $N_2$ -free basis gas composition during a 24-hours operation. It is the final output gas that excludes nitrogen and water. During the 24-hours continuous operation of experiment, 48% (at dry  $N_2$ -free basis) of hydrogen is obtained from the integration system at optimized conditions. Other major components are 35% carbon dioxide, 9% methane and 8% carbon monoxide. Using peanut shells as feedstock, the overall yield from this system is up to 6 wt% hydrogen and 32 wt% charcoal/activated carbon.

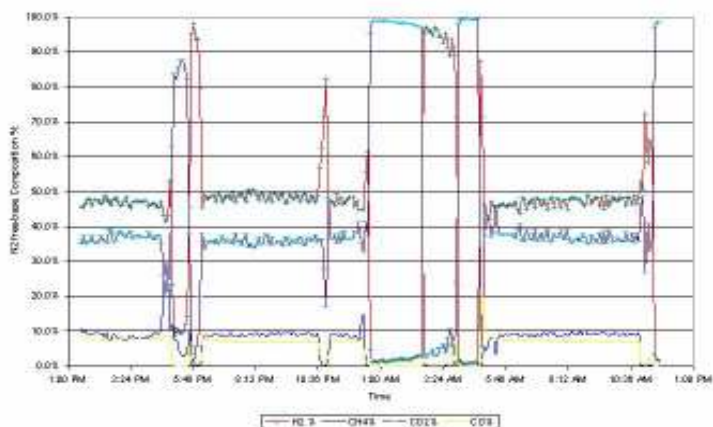


Figure 6 Dry  $N_2$ -free basis gas compositions via Time

The pyrolysis unit has produced char samples, which planned to use as the sequestration material. Figure 7 is the photo of sample char material.



Figure 7 Char material produced by the Pyrolyzer

Figure 8 is the result of investigation of the leaching examination of different chars, which are produced with different exit temperatures, from 400°C-900°C. This figure shows that the 400°C char has the potential of long term slow release of nutrients, hinting good candidate for a time-release fertilizer.

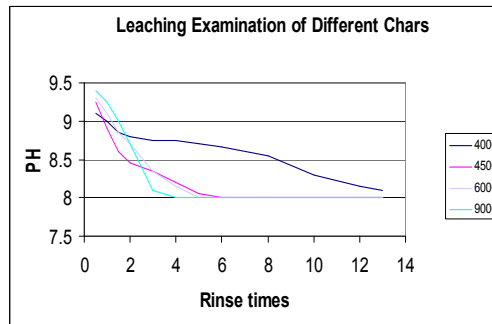


Figure 8 leaching examination of different chars.

Since the char around exit temperature 400°C is good to keep fertilizer time-release. We tested the fertilizer absorption of the char around this temperature (380°C- 420°C). Figure 9 shows that the 380°C-420°C chars have similar absorbability and 400°C char is little better.

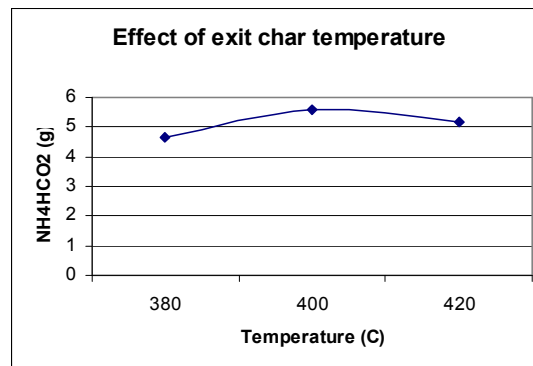


Figure 9 Effect of exit char temperature

The effect of char without NH<sub>4</sub>HCO<sub>3</sub> on plants are evaluated in this period. The evaluation of the fertilizer, NH<sub>4</sub>HCO<sub>3</sub> Char product, will be conducted later.

Figure 10 and figure 11 are the simple trials to explore the effect of three different chars on the plants. The two chars that applied in these experiments as fertilizer were

produces from peanut shell through two different processes. One char was made from our integrated hydrogen production process, another was from the traditional slow burning heap in a barrel, with limited oxygen. One group of plants that did not apply any char was used to compare with other two groups.



(a) No char applied



(b) Char made from slow burning process



(c) Char made from integrated hydrogen production process

Figure 10 Comparison of con plants with different chars applied as fertilizer

Corn plans were used as samples in figure 10. Figure 10 (a), (b) and (c) are photos of the corn plants, which applied no char, char with traditional slow burning process and our integrated process, respectively. All the seed were put down at the same time and three

groups of corn plants grew at the same conditions, except the char application. In the photos, the yellow sticks in the back are just over four feet, so that the no char group (fig.10 (a)) is approximately 2 feet, the char group (fig.10 (b)) made with a slow burning in the barrels at low temperature is approximately 3 feet and the char group (fig.10 (c)) made from integrated hydrogen production process is almost 4 feet.



(a) No char applied



(b) Char made from slow burning process



(c) Char made from integrated hydrogen production process

Figure 11 Comparison of vegetable plants with different chars applied as fertilizer

Vegetable plans were used as samples in figure 11. Figure 11 (a), (b) and (c) are photos of the vegetable plants, which applied no char, char with traditional slow burning process and our integrated process, respectively. All the seed were put down at the same time

and three vegetable plants grew at the same conditions, except the char application. In the photos, the plant with no char applied (fig.11 (a)) is approximately 12 inches, the plant with char (fig.11 (b)) made with a slow burning in the barrels at low temperature is approximately 20 inches and the plant with char (fig.11 (c)) made from integrated hydrogen production process is almost 28 inches.

Based on the site operation, a statistical result of system energy balance is summarized in table 1.

Table 1. System Energy Balance

Consumption	KJ	Recovery	KJ	Heat Sources	KJ
Biomass					
Preheating	76	Recovery I	250	External	280
Pyrolysis	121	Recovery II	362	Reactions	17
				Steam	
Bio-oil Preheating	38	Cooler I	48	recycling	32
Reforming	100	Cooler II	29		
Steam					
Superheating	675	Cooler III	28		
Syngas Preheating	49	Cooler IV	16		
Total	1059		733		329

The overall energy efficiency is about 61%. The major factor led to the lower energy efficiency than expected is mainly due to the low heat recovery efficiency.

## FUTURE PLANS

In the past year, we have finished the char and hydrogen production experiments, produced char samples, built the setup of bench scale experiments, and initiated the characteristic analysis of char products. The future works include the following tasks.

1. Testing, characterization of the time releasing fertilizer applied in soils.
2.  $\text{NH}_3\text{-CO}_2$  solidification process optimization
3. Further economic analysis

## CONCLUSIONS

1. The pilot scale hydrogen and char production tests have completed.
2. The bench scale equipment has been used for scrubbing CO<sub>2</sub> to for fertilizer.
3. The pilot scale facilities are installed and finished char and hydrogen production tests
4. Primary investigation to char characteristics has been done.
5. The effect of char without NH<sub>4</sub>HCO<sub>3</sub> was evaluated on growth of corn and vegetable.

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